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THE STRUCTURES OF FEROCAULIN, FEROCAULININ, FEROCAULIDIN, AND FEROCAULICIN

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A number of terpenoid coumarins have been isolated previously from the roots of *Ferula conocaula* Korov. [1-6]. From the roots of this plant collected in the village of Chashma, Leninabad oblast, TadzhSSR, we have isolated four new coumarin derivatives which we have called ferocaulin (I), ferocaulinin (II), ferocaulidin (III), and ferocaulicin (IV).

The UV spectra of substances (I-IV) show maxima characteristic for derivatives of 7-hydroxycoumarin, as was confirmed by the formation of umbelliferone (V) on the acid hydrolysis of (I-IV). The IR spectra of (I-III) show absorption bands due to the presence of aromatic nucleus, the carbonyl group of an α-pyrone and a carbonyl group in a six-membered ring, a double bond, and a hydroxy group.

Ferocaulin (I), with the composition $C_{24}H_{28}O_5$, has a mass spectrum [m/e 396 (M^+), 381 $(M-15)^+$, 378 $(M-H_2O)^+$, 235 $(M-ArO)^+$, 162 $(ArOH)^+$], similar to that of terpenoid coumarins of the iresane series [7, 8]. The composition of the terpenoid moiety ($C_{15}H_{24}O_2$), the presence in the PMR spectrum of the signals of four methyl groups (Table 1), and the nature of the fragmentation in the mass spectrum indicate that this moiety of ferocaulin has the iresane skeleton and contains hydroxy and carbonyl groups and a double bond.

The dehydrogenation of ferocaulin with selenium led to 1,2,5,6-tetramethylnaphthalene (VI), the formation of which confirms that (I) belongs to the terpenoid coumarins of the iresane series and shows that the carbonyl or the hydroxy group is present at C_6' [9-12]. The signal of the hemihydroxy proton of the PMR spectrum of (I) is found at 4.40 ppm (1 H, ΣJ = 10 Hz). The resonance of the latter in such a weak field as compared with other terpenoid coumarins having a double bond in the bicyclic terpene system — conferol [2], moschatol [13], feropolidin [14], and mogoltacin [15]— shows that the methine proton at the carbon to which the hydroxy group is attached is located close to the double bond. In view of the presence of an olefinic proton and a vinylmethyl group, and also of the multiplicity of the C_1'—CH_2OAr signal, the double bond in the terpenoid substituent must be located at C_2'—C_3'. Consequently, the hydroxy group is at C_4'. From the values of the CSs of the methyl groups (see Table 1), and also from the results of selenium dehydrogenation, the carbonyl group occupies the C_6' position. According to the facts given above, ferocaulin has the structure (I), as is confirmed by the passage from ferocaulin to conferdione (VII) [4] by oxidation with chromium trioxide. The product of this oxidation was a substance with the composition $C_{24}H_{26}O_5$, mp 150-152°C, M^+ 394, and with IR and PMR spectra identical with those of conferdione.

Ferocaulinin (II) has the composition $C_{24}H_{28}O_5$ (M^+ 396), and the mass spectrum shows the peaks of ions with m/e 378 $(M-H_2O)^+$, 363 $(M-H_2O-CH_3)^+$, 217 $(M-ArO-H_2O)^+$ and 162 $(ArOH)^+$.

A comparison of the compositions and UV, IR, PMR, and mass spectra of (I) and (II) shows that they are isomeric compounds. The PMR spectrum of ferocaulinin differs from that of (I) by the value of the CS and the half-width of the signals of the hemihydroxylic and olefinic protons, and also by the CSs of the methyl groups. In the spectrum of ferocaulinin the methine proton at the carbon atom to which the hydroxy group is attached is represented by a multiplet at 4.28 ppm (ΣJ = 17 Hz). The large value of the half width of the C_4'—M signal in (II) as compared with (I) shows that ferocaulinin is an epimer of ferocaulin, and the hydroxy

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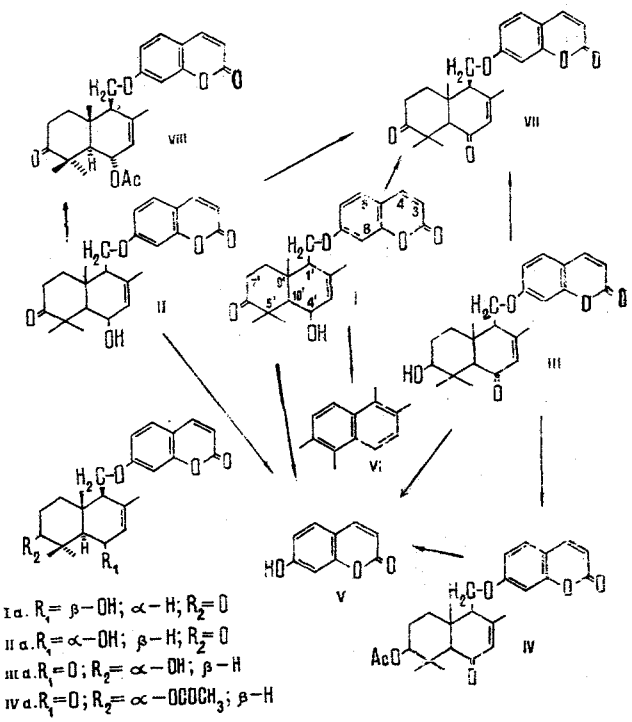
TABLE 1. Parameters of the PMR Spectra of (I-IV, VII, VIII) (δ, ppm; multiplicity, J, Hz)

Assignment	Compound					
	I	II	III	IV	VII	VIII
$3CH_3-C-$	1.17; s 1.36; s 1.46; s	0.96; s 1.29; s 1.31; s	1.00; s 1.14; s 1.18; s	1.02; s 1.10; s 1.21; s	1.24; s 1.27; s 1.39; s	1.02; s 1.10; s 1.20; s
$C_{2'}-CH_3$	1.75; ur $W_{\frac{1}{2}}$ =4.3	1.70; ur $W_{\frac{1}{2}}$ =4.3	1.90; ur $W_{\frac{1}{2}}$ =4.0	1.91; ur $W_{\frac{1}{2}}$ =4.0	1.94; ur $W_{\frac{1}{2}}$ =4.0	1.70; ur $W_{\frac{1}{2}}$ =4.2
$C_{4'}-OCOCH_3$	—	—	—	2.02; s	—	2.04; s
$C_{10'}-H$	—	—	2.58; s	2.52; s	2.47; s	—
$C_{1'}-H$	—	—	2.70; m	2.72; m	2.64; m	—
$C_{6'}-H$	—	—	3.30; ur $W_{\frac{1}{2}}$ = 7.0	4.60; ur $W_{\frac{1}{2}}$ = 7.0	—	—
$C_{1'}-CH_2-O-$	4.12; m	4.08; m	4.18; m	4.20; m	4.21; m	4.10; m
$C_{4'}-H$	4.40; ur $W_{\frac{1}{2}}$ =10.0	4.28; m $W_{\frac{1}{2}}$ =17.0	—	—	—	4.45; m $W_{\frac{1}{2}}$ =15.0
$C_{3'}-H$	5.70; ur $W_{\frac{1}{2}}$ =10.0	5.50; ur $W_{\frac{1}{2}}$ =6.0	5.82; ur $W_{\frac{1}{2}}$ =6.0	5.85; ur $W_{\frac{1}{2}}$ =6.0	5.91; ur $W_{\frac{1}{2}}$ =6.0	5.41; ur $W_{\frac{1}{2}}$ =6.0
C_3-H	6.20; d 9.5	6.20; d 9.5	6.18; d 9.5	6.21; d 9.5	6.22; d 9.5	6.21; d 9.5
C_8-H	6.87; m	6.79; m	6.78; m	6.74; m	6.78; m	6.78; m
C_6-H	6.87; m	6.79; m	6.78; m	6.74; m	6.78; m	6.78; m
C_5-H	7.37; d 9.0	7.34; d. 9.0	7.36; d. 9.0	7.38; d. 9.0	7.34; d. 9.0	7.32; d. 9.0
C_4-H	7.62; d. 9.5	7.60; d. 9.5	7.61; d. 9.5	7.60; d. 9.5	7.57; d. 9.5	7.57; d. 9.5

Note. s) singlet; d) doublet; q) quartet; m) multiplet; ur) unresolved signal.

group in it is oriented equatorially. In actual fact, when ferocaulinin was oxidized with chromium trioxide, conferdione was again obtained, which confirms the position of the hydroxy group at C_4' in ferocaulinin. The acetylation of (II) with acetic anhydride in pyridine led to the monoacetate (VIII), $C_{26}H_{30}O_6$, mp 140-142°C, M^+ 438, identical with conferin [5] in its physicochemical constants and spectral characteristics. Consequently, it may be concluded that ferocaulinin has the structure (II).

Ferocaulidin (III), with the composition $C_{24}H_{28}O_5$ (M^+ 396) also formed 1,2,5,6-tetramethylnaphthalene on selenium dehydrogenation, which shows that (III) belongs to the terpenoid coumarins of the iresane series and that the hydroxy group is located at C_6'. The position of the double bond in ferocaulidin at $C_2'-C_3'$ was established on the basis of the same facts as for (I) and (II). The UV spectrum of (III) has, together with other maxima characteristics for 7-hydroxycoumarin derivatives, absorption at 234 nm (log ε 4.18) due to the presence of an α,β-unsaturated carbonyl group. In addition, the signals of the olefinic and vinylmethyl protons have undergone a paramagnetic shift in comparison with (I) and (II). The same phenomenon was observed in the spectrum of conferdione [4]. These facts permit the conclusion that the double bond is present at $C_2'-C_3'$ and the carbonyl group at C_4'. The latter was also confirmed by the fact that the signal of the $C_{10}'-H$ proton is observed at 2.58 ppm and the $C_1'-H$ signal at 2.60 ppm. The oxidation of ferocaulidin with chromium trioxide yielded conferdione. On the basis of the facts given above, it may be concluded that ferocaulidin has the structure (III).



Ia. R_1 = β-OH; α-H; R_2 = O
IIa. R_1 = α-OH; β-H; R_2 = O
IIIa. R_1 = O; R_2 = α-OH; β-H
IVa. R_1 = O; R_2 = α-OCOCH$_3$; β-H

Ferocaulicin (IV), $C_{26}H_{30}O_6$ (M^+ 438), has in its IR spectrum the band of the carbonyl of an ester group, together with the absorption bands of the carbonyl of an α-pyrone and a carbonyl in a six-membered ring. The PMR spectrum of (IV) exhibits signals from the protons of an acetoxy group (s, 2.02 ppm, 3 H), and the signal from the hemihydroxylic proton exhibits a paramagnetic shift (Δδ 1.3 ppm) as compared with ferocaulidin. In addition, a small shift of the signals of the tertiary methyl groups is observed. These facts give grounds for assuming that ferocaulicin is the natural acetate of ferocaulidin. In actual fact, when ferocaulidin was acetylated, a monoacetate, $C_{26}H_{30}O_6$, was obtained the physicochemical constants and spectral characteristics of which were identical with those of ferocaulicin (IV).

The relative configurations of ferocaulin, ferocaulinin, ferocaulidin, and ferocaulicin were established on the basis of the following facts. The half-width of the signals of the hemihydroxylic (I-III) and hemiacylic (IV) protons in the PMR spectra of (I-IV) show that in ferocaulin and ferocaulidin the hydroxy group and in ferocaulicin the acetyl group have the axial orientation, and in ferocaulinin the hydroxy group is the equatorial orientation. The configurations of the other asymmetric centers, C_1', C_9', and C_{10}', are the same as in conferdione and conferin, as can be judged on the basis of the transformation into (VII). Thus, ferocaulin, ferocaulinin, ferocaulidin, and ferocaulicin have the relative configurations (Ia-IVa).

EXPERIMENTAL

The homogeneity of the substances was checked by thin-layer chromatography in Silufol plates in the chloroform–ethyl acetate (3:1) system. The PMR spectra (deuterochloroform) were recorded on a JNM-4H-100/100 MHz instrument with HMDS as internal standard (the values are given in the δ scale), the mass spectra were obtained on an MKh-1303 instrument with a glass system for direct introduction of the sample into the ion source, the IR spectra (tablets with KBr) on a UR-10 instrument, and the UV spectra on the Hitachi spectrophotometer in ethanol.

Isolation of the Coumarins. The comminuted air-dry roots (2.5 kg) of *F. conocaula* were extracted with ethanol (3 × 15 liters). The ethanolic solution was evaporated to 2.5 liters, diluted twofold with water, and extracted with ether (6 × 0.5 liter). Then the ether was distilled off to give 105 g (4.2%) of extractive substances, which were mixed with 100 g of silica gel, placed in a column containing silica gel (130 × 6 cm; 1700 g) and eluted with mixtures of hexane and chloroform with increasing amounts of the latter, 300-ml fractions being collected: 1-23 (4:1); 24-37 (3:1); 38-56 (2:1); 57-71 (1:1).

Ferocaulicin (IV). Evaporation of the solvent from fractions 12-17 yielded 0.64 g (0.025% on the weight of the dry plant) of colorless crystals, $C_{26}H_{30}O_6$, M^+ 438, mp 161-162.5°C (hexane–chloroform), $[\alpha]_D^{20}$ −120° (c 1.0; chloroform), R_f 0.38. IR spectrum: 1740, 1730, 1713, 1670, 1615, 1563, 1513 cm^{-1}. UV spectrum: λ_{max} 219, 235, 295, 324 nm (log ε 4.37, 4.27, 4.01, 4.20, respectively).

Ferocaulin (I). Fractions 27-30 yielded 0.3 g (0.011%) of acicular crystals, $C_{24}H_{28}O_5$, M^+ 396, mp 120-121°C (hexane–chloroform), $[\alpha]_D^{20}$ −20°C (c 1.0; ethanol), R_f 0.19. IR spectrum: 3510, 1730, 1714, 1618, 1560, 1518 cm^{-1}. UV spectrum: λ_{max} 217, 243, 253, 297, 326 nm (log ε 4.04, 3.45, 3.22, 3.84, 4.10, respectively).

Ferocaulinin (II). When fractions 40-44 of the eluate were concentrated, 0.42 g (0.16%) of colorless crystals deposited; $C_{24}H_{28}O_5$, M^+ 396, mp 84-86°C (hexane–diethyl ether), $[\alpha]_D^{20}$ −40° (c 1.0; ethanol), R_f 0.15. IR spectrum: 3460, 1733, 1712, 1617, 1560, 1517 cm^{-1}. UV spectrum: λ_{max} 216, 242, 253, 295, 325 nm (log ε 4.26, 3.76, 3.60, 3.97, 4.20, respectively).

Ferocaulidin (III). Fractions 59-64 yielded 0.39 g (0.015%) of a crystalline substance, $C_{24}H_{28}O_5$, M^+ 396, mp 75-77°C (hexane–ethyl acetate). $[\alpha]_D^{20}$ −75° (c 1.0; ethanol), R_f 0.10. IR spectrum: 3480, 1730, 1710, 1670, 1615, 1560, 1515 cm^{-1}. UV spectrum: λ_{max} 218, 234, 297, 325 nm (log ε 4.31, 4.18, 4.00, 4.22, respectively).

Acid Hydrolysis of Ferocaulin (V). A solution of 0.05 g of the substance in 3-4 ml of acetic acid was treated dropwise with 1 ml of concentrated sulfuric acid. After 30 min, the mixture was diluted with water and extracted with ether. The ethereal layer was treated with 5% caustic potash. The alkaline extract was acidified. A precipitate of umbelliferone (V) deposited with mp 230-232°C (from water).

Dehydrogenation of Ferocaulin (VI). A mixture of 0.1 g of the substance with 0.1 g of selenium was heated at 250-280°C for 2.5 h. The reaction product was dissolved in petroleum ether and the solution was filtered through a layer of alumina (activity grade II). The solvent was distilled off, giving 1,2,5,6-tetramethylnaphthalene (VI) with mp 112-113°C.

Oxidation of Ferocaulin (VII). A solution of 0.1 g of chromium trioxide in 2 ml of water was added dropwise to a solution of 0.1 g of the substance in 10 ml of acetone. After 20 min, the mixture was diluted with water and was treated with ether. The ethereal solution was washed with water, dried with sodium sulfate, and evaporated. This yielded conferdione (VII), $C_{24}H_{26}O_5$, M^+ 394, mp 151-152°C (hexane–diethyl ether).

Acetylation of Ferocaulinin (VIII). A solution of 0.11 g of the substance in 2 ml of acetic anhydride and 2 ml of pyridine was heated on the water bath. After the solvent had been driven off, conferin (VIII), $C_{26}H_{30}O_6$, mp 140-142°C (hexane–diethyl ether) was obtained.

The oxidation of ferocaulinin (VII) was performed in a similar manner to the oxidation of ferocaulin. After the usual working up, the reaction mixture yielded a substance with mp 151-152°C. A mixture of this substance with the conferdione from ferocaulin showed no depression of the melting point.

Acetylation of Ferocaulidin (IV). After 0.09 g of the substance had been kept in 1 ml of a mixture of acetic anhydride and pyridine (1:1) at 20°C for 20 h, it was diluted with 10 ml of water and extracted with ether (5 × 2 ml), the ethereal solution was washed with 8% HCL (5 × 2 ml) and then with water (5 × 2 ml), dried with anhydrous sodium sulfate, and evaporated. This ferocaulidin acetate (IV), $C_{26}H_{30}O_6$, M^+ 438, mp 161-162.5°C (hexane–chloroform), which gave no depression of the melting point in admixture with ferocaulicin, was obtained.

The oxidation of ferocaulidin (VII) was performed by the above-described method. The substance isolated, with mp 151-152°C, proved to be identical with conferdione from ferocaulin (from its melting point and IR and NMR spectra).

SUMMARY

From the roots of *Ferula conocaula* Korov. four new terpenoid coumarins have been isolated: ferocaulin (I), ferocaulinin (II), ferocaulidin (III), and ferocaulicin (IV).

On the basis of chemical reactions and spectral characteristics, and also conversion into conferdione, the structures and relative configurations (Ia-IVa) have been established for them.

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STRUCTURES OF CAUFERIN AND CAUFERIDIN

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Continuing a study of the coumarins of the roots of *Ferula conocaula* Korov. [1], we have isolated two new terpenoid coumarins which we have called cauferin (I) and cauferidin (II).

Cauferin (I) has the composition $C_{24}H_{30}O_5$, M^+ 398, mp 104-106°C, $[\alpha]_D^{23}$ −50° (c 1.0; $CHCl_3$). The UV spectrum of (I) is characteristic for a 7-hydroxycoumarin chromophore. The IR spectrum shows absorption bands due to the presence of an aromatic nucleus, the carbonyl of an α-pyrone, and a hydroxy group. The terpenoid moiety of cauferin has the composition $C_{15}H_{25}O_2$, both oxygen atoms in it being in the form of secondary hydroxy group. This is confirmed by the PMR spectrum of the diacetyl derivative of cauferin (III), $C_{28}H_{34}O_7$, M^+ 482.

The mass spectrum of (I) shows the peaks of ions with m/e 398 (M^+), 380 $(M - H_2O)^+$, 237 $(M - ArO)^+$, 219 $(M - ArO - H_2O)^+$, 201 $(M - ArO - 2H_2O)^+$, 162 $(ArOH)^+$ which are characteristic for terpenoid coumarins of the iresane series [2-4]. With the given composition and the characteristics of the IR, PMR, and mass spectra, the sesquiterpene fragment of cauferin must have a bicyclic structure. This is also shown by the formation of umbelliferone (IV) and of a tetramethylnaphthalene (V) on the dehydrogenation of (I) with selenium. The formation of the latter compound enables us to consider that the sesquiterpene moiety is represented by an iresane structure and that one of the hydroxy groups is present in position 6' [5-7].

On the basis of what has been said, and taking into account the fact that the PMR spectrum of (I) (Table 1) has signals on the protons of three methyl groups (attached to quaternary carbon atoms) and of $-CH_2-OAr$ and $>C=CH_2$ groups, and also the signal of a hemihydroxylic proton, the sesquiterpene residue can be assigned the following partial structure:

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